

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-214009

(43)Date of publication of application : 06.08.1999

(51)Int.Cl.

H01M 4/60

H01M 4/02

H01M 4/04

(21)Application number : 10-026628

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(22)Date of filing : 23.01.1998

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## (54) REDOX ACTIVE ELECTRODE AND MANUFACTURE THEREOF

## (57)Abstract:

PROBLEM TO BE SOLVED: To improve characteristic such as charging and discharging speed, while promoting redox reaction of the conductive polymer by composing a composition including a redox reactive conductive polymer and a reaction auxiliary material redox reactive in an electrical potential range showing the oxidization and reduction responses of the conductive polymer.

SOLUTION: As a conductive polymer,  $\pi$  electron conjugated polymer such as polyaniline, polypyrrole and polythiophene is used. Redox reactive electrical potential region of the conductive polymer correspond to the electrical potential region in which redox current is observed by cyclic voltamogram, and the electrical potential region differs according to the kind of the conductive polymer and the kind of the substituent group. As a reaction auxiliary material, (1) ions of heavy metal, or transition metal, metal acid, metal complex (2) heavy metal or transition metal, (3) metal oxide, metal sulfide or the like (4) hydroquinone derivative (5) viologen derivative (6) organic metal compound such as metallocene, (7) organism related material are used.

## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

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## CLAIMS

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[Claim(s)]

[Claim 1] (A) The redox active electrode characterized by the bird clapper from the constituent with which the conductive polymer compound in which oxidation reduction is possible, and the (B) aforementioned conductive polymer compound contain the reaction adjuvant in which oxidation reduction is possible in the potential range which shows an oxidization response and a reduction response.

[Claim 2] The redox active electrode according to claim ① whose conductive polymer compound in which the oxidation reduction of the above (A) is possible is what has a substituent combinable with the reaction adjuvant of the above (B).

[Claim 3] The redox active electrode according to claim ① or ② which is a thing containing the macromolecule in which the aforementioned constituent has a macromolecule and/or coordination capacity with ion-exchange capacity.

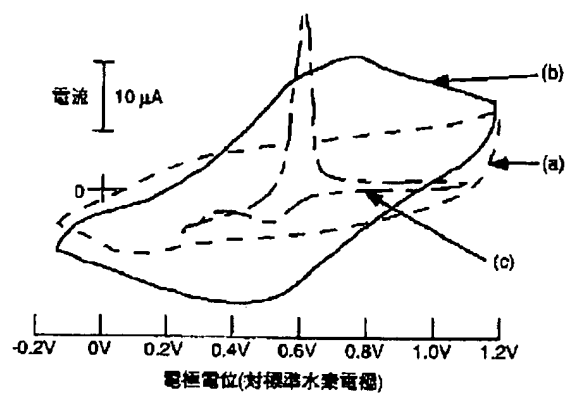
[Claim 4] (A) The process of the redox active electrode characterized by the conductive polymer compound in which oxidation reduction is possible, and the (B) aforementioned conductive polymer compound mixing the reaction adjuvant in which oxidation reduction is possible in the potential range which shows an oxidization response and a reduction response.

[Claim 5] (a) The process of the redox active electrode characterized by the (b) aforementioned conductive polymer compound carrying out the polymerization of the monomer which can form the conductive polymer compound in which oxidation reduction is possible to the bottom of coexistence of the reaction adjuvant in which oxidation reduction is possible in the potential range which shows an oxidization response and a reduction response.

[Claim 6] The process of the redox active electrode characterized by being immersed into the solution which contains the reaction adjuvant in which oxidation reduction is possible in the potential range the aforementioned conductive polymer compound indicates an oxidization response and a reduction response to be for the electrode with which the conductive polymer compound in which oxidation reduction is possible is covered.

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the redox active electrode using the conductive polymer compound in which oxidation reduction is possible, and its process.

[0002]

[Description of the Prior Art] Charge storage capacity also has the pi-electron conjugated-system conductive polymer compound in which oxidation reduction, such as the poly aniline and polypyrrole, is possible while it shows high electronic-conduction nature. As a material, it is flexible, and these conductive polymer compounds can be easily cast to a thin film etc., and are cheap. Furthermore, after use can do processing simply by incineration or the chemical treatment, and it is hard to start environmental pollution. Moreover, the design in molecule level is also possible by introduction of a substituent etc. For this reason, research and development of the redox active electrode using the conductive polymer compound in which oxidation reduction is possible are done, and the poly aniline electrode is put in practical use as a positive electrode for lithium secondary batteries until now in recent years.

[0003] Moreover, the poly aniline, and 2, 5-dimercapto - When the complex which consists of organosulfur compounds, such as 1, 3, and 4-thiadiazole, is used as a positive-electrode material of a lithium secondary battery, it is reported that the very high energy density to which the oxidation-reduction reaction of an organosulfur compound is promoted with a conductive polymer compound, and exceeds kg in 800Whs /is obtained [Nature, vol.373, p.598-600 (1995)].

[0004] Furthermore, by combining this complex positive electrode with a copper charge collector, the discharge voltage stabilized more is obtained as compared with the case where it combines with a carbon electrode, high-speed electric discharge is also attained, further, it excels also in the stability in the charge and discharge of a repeat, and 250 times or more of repeat charges and discharges become possible. Copper [ some ] is eluted, these effects form an organosulfur compound and a complex, and it is guessed that they are what shows an electronic-transition reaction with this quicker complex.

[0005] However, in the former, the attempt which improves properties, such as charge-and-discharge speed of the redox active electrode which consists of a conductive polymer compound in which oxidation reduction is possible, is not yet made at all by promoting the oxidation-reduction reaction of a conductive polymer compound using another matter.

[0006]

[Problem(s) to be Solved by the Invention] The purpose of this invention promotes the oxidation-reduction reaction of a conductive polymer compound by the reaction adjuvant in which oxidation reduction is possible, and is in the point of offering the redox active electrode by which properties, such as charge-and-discharge speed, were improved by this, and its manufacture method.

[0007] In order that this invention persons may raise properties, such as charge-and-discharge speed of an electrode, they discover that the oxidation-reduction reaction of the conductive polymer compound which exists on an electrode can be remarkably promoted using another matter that nobody considered until now, and came to complete this invention.

[0008]

[Means for Solving the Problem] It is related with the redox active electrode characterized by the bird clapper from the constituent with which the conductive polymer compound in which (A) oxidation reduction is possible, and the (B) aforementioned conductive polymer compound contain the reaction adjuvant in which oxidation reduction is possible in the potential range which shows an oxidization response and a reduction response the first of this invention.

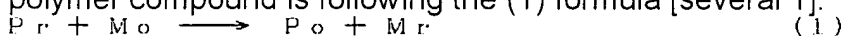
[0009] The aforementioned constituent of this invention may contain a high molecular compound with a macromolecule and/or coordination capacity with ion-exchange capacity.

[0010] The second (the 1st manufacture method) of this invention is related with the process of the redox active electrode characterized by the conductive polymer compound in which (A) oxidation reduction is possible, and the (B) aforementioned conductive polymer compound mixing the quality of a reaction assistant in which oxidation reduction is possible in the potential range which shows an oxidization response and a reduction response.

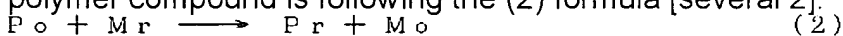
[0011] The third (the 2nd manufacture method) of this invention is related with the process of the redox active electrode characterized by the (b) aforementioned conductive polymer compound carrying out the polymerization of the monomer which can form the conductive polymer compound in which (a) oxidation reduction is possible to the bottom of coexistence of the quality of a reaction assistant in which oxidation reduction is possible in the potential range which shows an oxidization response and a reduction response.

[0012] The fourth is related with the process of the redox active electrode characterized by being immersed into the solution which contains the quality of a reaction assistant in which oxidation reduction is possible in the potential range the aforementioned conductive polymer compound indicates an oxidization response and a reduction response to be for the electrode with which the conductive polymer compound in which the oxidation reduction of this invention is possible is covered.

[0013] If the aforementioned conductive polymer compound adds the quality of a reaction assistant (M) in which oxidation reduction is possible to the conductive polymer compound (P) in which oxidation reduction is possible in the potential range which shows an oxidization response and a reduction response, the oxidation-reduction reaction of a conductive polymer compound (P) will be promoted, and the increase in oxidation reduction current will be observed. For this, it sets in the oxidization process of a conductive polymer compound, and the reductant (Pr) of a conductive polymer compound is following the (1) formula [several 1].



It is alike, and it follows, oxidizes by the oxidant (Mo) of the aforementioned quality of a reaction assistant, becomes an oxidant (Po), it sets in reduction process, and the oxidant (Po) of a conductive polymer compound is following the (2) formula [several 2].



It is alike, and it follows, is returned by the reductant (Mr) of the aforementioned quality of a reaction assistant, becomes a reductant (Pr), and is because the oxidation-reduction reaction of a conductive polymer compound is performed via the aforementioned quality of a reaction assistant.

[0014] On these specifications, it is used in the meaning "an oxidant and a reductant exist and reduction of an oxidant and oxidization of a reductant are as possible as "oxidation reduction is possible"", and the matter in which oxidation reduction is possible means an oxidant or a reductant so that clearly from the above explanation.

[0015] As a conductive polymer compound used by this invention, although pi-electron conjugated-system high molecular compounds, such as the poly aniline, polypyrrole, and the poly thiophene, etc. are mentioned, if it is the conductive polymer compound in which oxidation reduction is possible, it will not be restrained especially.

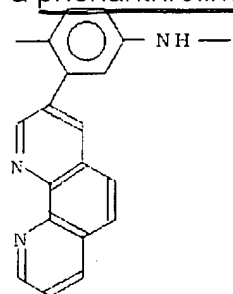
[0016] As for the conductive polymer compound in which such oxidation reduction is possible, it is desirable to have the substituent combined with the aforementioned reaction adjuvant. When such a substituent and the aforementioned reaction adjuvant form ionic bond, coordinate bond, hydrogen bond, etc., the aforementioned reaction adjuvant is further held by the conductive polymer compound

top at stability and high concentration.

[0017] Here, as a substituent on the aforementioned conductive polymer compound combined with the aforementioned reaction adjuvant, the substituent of ionic bond nature substituent, coordinate bond nature substituent, and ion-coordinate bond nature and hydrogen bond nature is mentioned. As an ionic bond nature substituent,  $\text{-SO}_3^-$ , the fourth class ammonium cation machine (a pyridinium cation machine is included), etc. are mentioned. (b) As a substituent of (b) coordinate bond nature NR One R2 (R1 and R2 Express Basis Chosen from Group Which Consists of Univalent Organic Machines, Such as Hydrogen and Alkyl Group); - Ethylenediamine, A substituent with amine system multidentate-ligand residues, such as a propylenediamine, a diethylenetriamine, and a triethylenetetramine; A pyridyl machine, A PIPRIJIRU machine, a TAPIRIJIRU machine, a phenan TORORIRU machine, a pyrazyl machine, a pyrimidyl machine, pyridazyl machine; -PR three R4 (R3 and R4) A substituent with ether system multidentate-ligand residues, such as a substituent; glyme which has the Lynn system multidentate-ligand residues, such as a die force, and it expresses the basis chosen from the group which consists of univalent organic machines, such as hydrogen and an alkyl group; A porphyrin, A substituent with annular ligand residues, such as a phthalocyanine; A carbon carbon double bond (ethylenic linkage), Carbon carbon triple bond (acetylenic linkage),  $>\text{C}=\text{O}$ ,  $>\text{C}=\text{N}$ -,  $\text{-CN}$ , Coordination Nature Substituent Which Has Unsaturated Bonds, Such as  $\text{NO}$ ,  $>\text{S}=\text{O}$ -,  $\text{-S-CN}$ ,  $\text{-NCO}$ , and  $\text{-NCS}$ ; - Phenyl Group and Boron, Complex annular coordination nature substituent; -NC containing Lynn, sulfur, a silicon, etc. is mentioned. as a (c) ion-coordinate bond nature substituent - A coordination nature substituent with  $\text{COO}^-$ -,  $\text{-S-}$ , acetylacetonate, a GURIOKISHI mate, glycinate, a dithio carbamate, cyclopentadienyl, a PIRORETO residue, etc. is mentioned. (d) As a substituent of hydrogen bond nature, the substituent of  $\text{-OH}$ -,  $\text{-SH}$ -,  $\text{-NH}_2$  (R shows univalent organic machines, such as hydrogen or an alkyl group),  $\text{-PH}$ -,  $\text{-COOH}$ -,  $\text{-CN}$ -,  $\text{-PO}$ -,  $\text{-F}$ -,  $\text{-Cl}$ -, and  $\text{-NO}_2$  grade is mentioned.

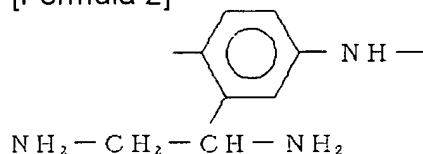
[0018] One example of the form where the aforementioned substituent is introduced into the conductive polymer compound is shown.

[0019] It is [Formula 1] which is as the following formula when a conductive polymer compound uses a phenanthroline as a source of a substituent by the poly aniline.

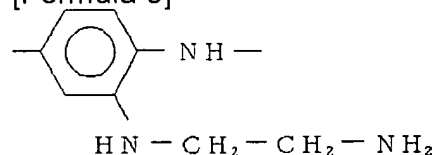


[0020] By the poly aniline, when a conductive polymer compound uses ethylenediamine as a source of a substituent, it presents two kinds of following introductory states.

[Formula 2]



[Formula 3]



[0021] In this invention, the aforementioned quality of a reaction assistant which has oxidation reduction potential to the potential field in which the oxidation reduction of this compound is possible

in a conductive polymer compound which was mentioned above, and in which oxidation reduction is possible is added.

[0022] In the case of potential field [ , for example, the sulfonation poly aniline shown with the curve (a) of drawing 1 , by which oxidation reduction current is observed with a cyclic voltamogram, the potential field in which the oxidation reduction of a conductive polymer compound is possible corresponds to range [ of -0.1-+1.2v ] mostly on the basis of a normal hydrogen electrode, and differ according to the kind of conductive polymer compound, and the kind of substituent.

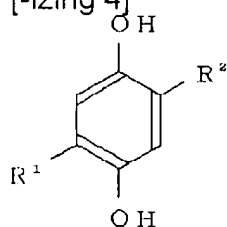
[0023] Moreover, the oxidation reduction potential of the aforementioned quality of a reaction assistant is the average potential of the oxidization summit potential of the quality of a reaction assistant and reduction summit potential in the cyclic voltamogram obtained using the electrode which covered the conductive polymer compound which is going to promote oxidation reaction. This average potential is not necessarily in agreement with the same average potential obtained using the electrode which has not covered the conductive polymer compound.

[0024] When this invention persons had the oxidation reduction potential of the aforementioned quality of a reaction assistant in the potential field in which the oxidation reduction of a conductive polymer compound is possible, it found out that an electronic-automatic-exchange reaction occurred between a conductive polymer compound and the quality of a reaction assistant, and a part of oxidation-reduction reaction [ at least ] of a conductive polymer compound was performed via the aforementioned quality of a reaction assistant, consequently the oxidation-reduction reaction of a conductive polymer compound was promoted.

[0025] There are what oxidizes like the poly aniline and becomes a cation type, and a thing which is returned like a sulfonation poly aniline and becomes an anion type in the conductive polymer compound in which oxidation reduction is possible. Although the potential field in which the oxidation reduction of these conductive polymer compounds is possible changes with kinds of substituent introduced on the kind of conductive polymer compound, or the macromolecule, it is usually included on the basis of a normal hydrogen electrode at potential within the limits of -1.5-+1.5v. Therefore, the aforementioned quality of a reaction assistant usually has oxidation reduction potential in potential within the limits of -1.5-+1.5v on the basis of a normal hydrogen electrode according to the potential field in which the oxidation reduction of a conductive polymer compound is possible. *not enhances*

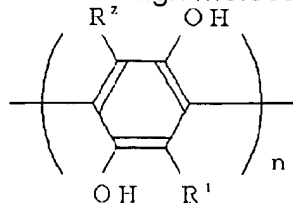
[0026] The following can be mentioned as the aforementioned quality of a reaction assistant.

(1) Ion kind  $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{V}^{2+}$ ,  $\text{Sn}^{2+}$ , The metal ion which consists of the heavy metal or transition metals other than alkali metal, such as  $\text{Sm}^{2+}$ , and alkaline earth metal,  $\text{MnO}$  -- four - etc. -- a metal -- an acid -- ion -- [ -- Fe -- ( -- CN -- ) -- six -- ] -- three - [ -- Ru -- ( -- CN -- ) -- six -- ] -- three - [  $\text{Ir}(\text{Cl})_6$  ]  $2^-$ , [  $\text{W}(\text{CN})_8$  ]  $3^-$ , [  $\text{Ru}(\text{NH}_3)_6$  ]  $3^+$ , [  $\text{Co}(\text{bpy})_3$  ]  $2^+$ , [ion [ metal complex ] (2) metal Cu, such as Ru (bpy)  $3]^{2+}$  (bpy; bipyridine), Heavy metal, such as Fe, Ag, aluminum, nickel, Co, Zn, and Ti, or the transition-metals (3) inorganic compounds  $\text{MnO}_2$ ,  $\text{NiO}_2$ , and  $\text{CoO}_2$ ,  $\text{V}_2\text{O}_5$ , the metallic oxide of  $\text{Nb}_2\text{O}_5$  grade, The hydroquinone derivative shown by the inorganic compound (4) following general formulas (1), such as metallic sulfide of  $\text{TiS}_2$  and  $\text{MoS}_2$  grade, and a metal selenide of  $\text{NbSe}_3$  grade, [-izing 4]



( 1 )

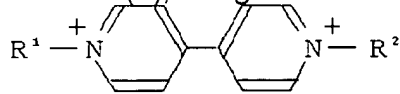
And the high molecular compound shown by the following general formula (2) [-izing 5]



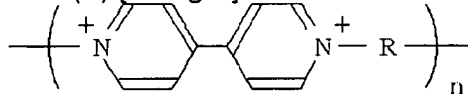
( 2 )

n expresses two or more integers and R<sup>1</sup> and R<sup>2</sup> express the basis chosen respectively independently of the group which consists of a univalent organic machine of hydrogen and alkyl groups (a methyl group, ethyl group, etc.) among [a general formula (1) and (2).]

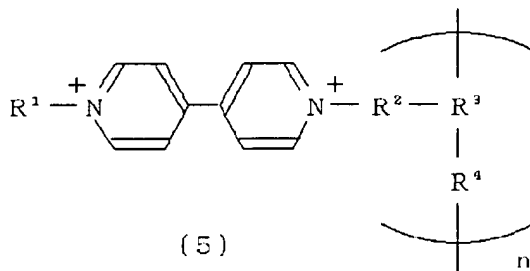
(5) The high molecular compound shown by the viologen derivative shown by the following general formula (3), the general formula (4), and (5) [izing 6]



(3)



(4)



(5)

n expresses two or more integers and R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> express the basis chosen respectively independently of the group which consists of a univalent organic machine of hydrogen and alkyl groups (a methyl group, ethyl group, etc.) among [a general formula (3), (4), and (5).]

(6) Organometallic compounds, such as a metallocene whose central metals are Fe, Mo, Mn, etc.

(7) A living body related substance like a ubiquinone, NADH, and FAD.

[0027] As opposed to the metal ion which carried out [aforementioned] instantiation the oxidation reduction potential of alkaline-earth-metal ion, such as alkali-metal ion, such as Li<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup>, and calcium<sup>2+</sup>, Ba<sup>2+</sup> It has separated from the potential range of -1.5-+1.5v on the basis of the normal hydrogen electrode. To the usual conductive polymer compound, it is inactive electrochemically, the conductive polymer compound in which oxidation reduction is possible cannot usually be oxidized or returned, and, therefore, the oxidation-reduction reaction of a conductive polymer compound cannot be promoted. This is clearer than supporting electrolytes which are inactive electrochemically, such as LiClO<sub>4</sub> electrolyte, are used in the research using the poly aniline which has the potential field in which oxidation reduction is possible on the basis of a normal hydrogen electrode in potential within the limits of -1.5-+1.5v, polypyrrole, and those sulfonated "self-dope type" conductive polymer compounds.

[0028] When (i) ion kind is used as quality of a reaction assistant, the redox active electrode concerning this invention An ion kind, In having the oxidant of a conductive polymer compound or reductant in which oxidation reduction is possible, or the substituent which this conductive polymer compound combines with an ion kind, this substituent combines. When an ion kind is stably held by high density on the conductive polymer compound in which oxidation reduction is possible, An ion kind is embraced. control of oxidation reduction potential is attained or Or an oxidation state, High reactivity, high selectivity, and high stability are given -- the solubility over a catalyst changes. (ii) When a metal and an inorganic compound are used, to a physical and chemically stable top Since composition of the material appropriate for the purpose is easy for an organic compound when it becomes possible when it uses as an electrode for cells to raise the energy density per unit weight and an organic compound (iii) is used, When versatility and reactivity are given and the (iv) organometallic compound is used, can sort out the feature which the above-mentioned inorganic one and an organic compound have, and since an organometallic compound is quick, a self-electronic-transition reaction it is possible to raise a promotion operation of an electronic-transition reaction, and when (v) living body related substance is used, it is possible to realize high selectivity to the reactivity

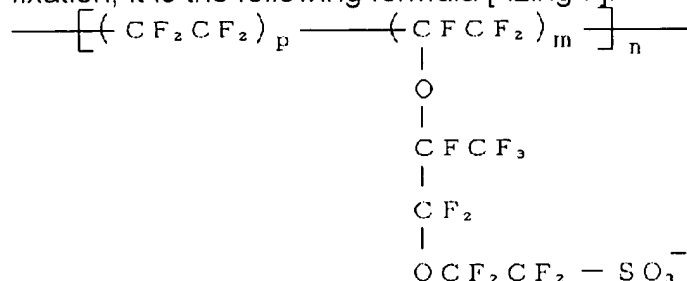


which a biological substance has, and high conversion ability -- etc. -- it is characteristic [0029] Thus, the features differ and the electrode built over this invention according to the kind of quality of a reaction assistant can choose the electrode which has the suitable feature according to a use etc.

[0030] By this invention, the mixture of the conductive polymer compound and the aforementioned quality of a reaction assistant in which oxidation reduction is possible can be used as an electrode in the state where it formed on charge collectors, such as direct or carbon, copper, aluminum, and conductive transparent glass.

[0031] The redox active electrode concerning this invention may contain additives, such as an electrolyte and an organic or inorganic sulfur compound, by the aforementioned reaction adjuvant within quantitative limits by which the oxidation-reduction reaction of the conductive polymer compound in which oxidation reduction is possible is fully promoted.

[0032] Moreover, in order to perform high-concentration-izing of reaction adjuvant, stabilization, and fixation, it is the following formula [-izing 7].



It can come out and polyethers, such as ion exchange resin, such as Nafion expressed, and a polyethylene oxide, a polypropylene oxide, can be made to contain.

[0033] It is possible to fix the aforementioned reaction adjuvant to high concentration stably near [ in which oxidation reduction is possible ] the conductive polymer compound including the macromolecule in which the redox active electrode concerning this invention has ion-exchange capacity, when the aforementioned reaction adjuvant is an ion kind. Moreover, when the redox active electrode concerning this invention contains the macromolecule (coordination nature macromolecule) which has ligands, such as the ether and a pyridine, while configuring in the aforementioned reaction adjuvant and contributing to the high-concentration-izing, stabilization, and fixation, high mobility is given to the aforementioned reaction adjuvant in the interior of an electrode. Furthermore, the mechanical strength of the redox active electrode concerning this invention increases by adding these third components. According to these effects, the property of the redox active electrode concerning this invention of an electrode improves as compared with the case where these third components are not included.

[0034] The redox active electrode of this invention can be manufactured with either of the three above-mentioned methods. When the quality of a reaction assistant is an ion kind in the aforementioned method, an ion kind is used with the form of a compound including an ion kind. For example, when an ion kind is metal ion Mn[ , such as Cu<sup>2+</sup> and Fe<sup>3+</sup>, ]+, the compound expressed with MxA(ies) (A is the anion of m \*\* among a formula, and it is nx=my), such as CuCl<sub>2</sub> and FeCl<sub>3</sub>, is used as an oxidation-reduction reaction medium. On the other hand, although a metal salt including these ion kinds can be used as quality of a reaction assistant when ion kinds are anions, such as metal acid ion, lithium salt is desirable when using for a lithium cell or a lithium ion battery the redox active electrode especially built over this invention.

[0035] Moreover, a metal ion can be returned and a desired metal can also be obtained, after using the compound containing this metal ion, when reaction adjuvant is a metal.

[0036] When manufacturing the redox active electrode built over this invention by the 1st manufacture method of this invention, the method of mixing the aforementioned reaction adjuvant and the conductive polymer compound in which oxidation reduction is possible in the state of a solid-state (powder), the method of applying this to a charge collector if needed, and subsequently removing a solvent, after mixing these in the state where it was made to dissolve in a solvent, etc. are adopted.

[0037] moreover, in case the redox active electrode built over this invention by the 2nd manufacture method of this invention is manufactured It is under [ solution / which dissolves and contains the aforementioned reaction adjuvant and the monomer of the conductive polymer compound in which oxidation reduction is possible ] setting. After carrying out the polymerization of the aforementioned monomer, inserting a charge collector into the method of drying after that, or the solution which dissolves and contains the aforementioned reaction adjuvant and the monomer of the conductive polymer compound in which oxidation reduction is possible and carrying out electrolytic polymerization of the monomer in a solution on this charge collector, the method of removing a solvent etc. is adopted.

[0038] In case the redox active electrode built over this invention by the 3rd manufacture method of this invention manufactures, it is immersed into the solution which contains the reaction adjuvant in which oxidation reduction is possible in the potential range the aforementioned conductive-polymer compound indicates an oxidization response and a reduction response to be for the electrode with which the conductive-polymer compound in which oxidation reduction is possible was covered, or the method of incorporating reaction adjuvant in a conductive-polymer compound by meanses, such as electrolyzing using the aforementioned electrode, is adopted.

[0039] Electrodes, such as a metal, a metal acid compound, and carbon, can be used for the redox active electrode concerning this invention as a charge collector.

[0040]

[Example] Although an example is given to below and this invention is explained to it, thereby, this invention is not limited at all.

[0041] The PAS covering GC electrode with a thickness of about 0.25 micrometers was created by drying the water-methanol mixed solution (1:1 water : methanol = capacity factor) containing sulfonation poly ANIN (conductive organic high-molecular-compound-AS) of example 17.5mM ( $M = \text{mol/dm}^3$ ) after 2microl cast on a glassy-carbon (GC) electrode (area;  $0.07\text{cm}^2$ ) for 1 hour. When potential was linearly increased or decreased at the rate of 50 mV/sec and was electrolyzed among -0.1-+1.2 volts on the basis of the normal hydrogen electrode in the (propylene carbonate PC) solution which dissolved  $\text{LiClO}_4$  for this electrode 0.1M as a supporting electrolyte, the cyclic voltamogram (current-voltage curve) shown with the curve (a) of drawing 1 was obtained.

[0042] Subsequently,  $\text{LiClO}_4$  was moved into PC solution (it considers as reaction adjuvant and metal ion  $\text{Cu}^{2+}$  is included) which dissolved 0.1M, having used  $\text{Cu}(\text{ClO}_4)_2$  as a reaction adjuvant formation material as 1mM and the supporting electrolyte for the PAS covering GC electrode after electrolysis, it electrolyzed like the above, and the cyclic voltamogram shown with the curve (b) of drawing 1 was obtained .

[0043] When it electrolyzed in PC solution which contains  $\text{Cu}(\text{ClO}_4)_2$  using GC electrode which has not covered the PAS thin film, the cyclic voltamogram shown with the curve (c) of drawing 1 was obtained.

[0044] In a curve (a), oxidation reduction is possible for PAS in [ potential ] -0.1-+1.2v on the basis of a normal hydrogen electrode. The oxidation reduction potential of  $\text{Cu}^{2+}$  in a PAS covering GC electrode was observed by 0.6v on the basis of the normal hydrogen electrode. When curvilinear [ of drawing 1 ] (a) - (c) is compared, the oxidation reduction current value [a curve (b)] obtained by electrolyzing the solution which contains metal ion  $\text{Cu}^{2+}$  using a PAS covering GC electrode is larger than the current value which doubled the current value observed with the curve (a) and the curve (c). This shows metal ion  $\text{Cu}^{2+}$  working as quality of a reaction assistant, and promoting the oxidation-reduction reaction of PAS which is a conductive polymer compound.

[0045] Moreover, when it moved into PC solution which does not contain  $\text{Cu}^{2+}$  which dissolved  $\text{LiClO}_4$  for the electrode after obtaining the cyclic voltamogram shown with the curve (b) of drawing 1 0.1M as a supporting electrolyte and having been electrolyzed like the above, larger oxidation reduction current value than the current value which doubled (c) with the curve (a) like the curve (b) was observed.

[0046] By electrolyzing in the solution which dissolved reaction adjuvant from the above thing using the electrode which covered the conductive polymer compound in which oxidation reduction is possible shows that reaction adjuvant is incorporated in a conductive polymer compound electrode,

and it is fixed stably, and the redox active electrode which consists of the reaction adjuvant which promotes the conductive polymer compound in which oxidation reduction is possible, and its oxidation-reduction reaction is obtained.

[0047] Except having replaced with example 2PC and having used the mixed solvent (PC:EC=1:1, weight ratio) of PC and ethylene carbonate (EC), it electrolyzed like the example 1 and curvilinear [ of [drawing 2](#) ] (a) - (c) was obtained, respectively. In a curve (a), oxidation reduction is possible for PAS in [ potential ] -0.1~+1.2v on the basis of a normal hydrogen electrode. The oxidation reduction potential of  $\text{Cu}^{2+}$  in a PAS covering GC electrode was observed by 0.6v on the basis of the normal hydrogen electrode. When curvilinear [ of [drawing 2](#) ] (a) - (c) is compared, the oxidation reduction current value [a curve (b)] obtained by electrolyzing the solution which contains metal ion  $\text{Cu}^{2+}$  using a PAS covering GC electrode is larger than the current value which doubled the current value observed with the curve (a) and the curve (c). This shows metal ion  $\text{Cu}^{2+}$  working as quality of a reaction assistant, and promoting the oxidation-reduction reaction of PAS which is a conductive polymer compound. Moreover, when it moved into the PC+EC mixed solution which does not contain  $\text{Cu}^{2+}$  which dissolved  $\text{LiClO}_4$  for the electrode after obtaining the cyclic voltamogram shown with the curve (b) of [drawing 2](#) 0.1M as a supporting electrolyte and having been electrolyzed like the above, larger oxidation reduction current value than the current value which doubled (c) with the curve (a) like the curve (b) was observed.

[0048] Except having replaced with example 3Cu ( $\text{ClO}_4$ )<sub>2</sub>, and having used  $\text{AgClO}_4$ , it electrolyzed like the example 1 and curvilinear [ of [drawing 3](#) ] (a) - (c) was obtained, respectively. From the curve (b), the oxidation reduction potential of  $\text{Ag}^+$  in a PAS covering GC electrode was observed by 0.8v on the basis of the normal hydrogen electrode. When curvilinear [ of [drawing 3](#) ] (a) - (c) is compared, the oxidation reduction current value [a curve (b)] obtained by electrolyzing the solution which contains metal ion  $\text{Ag}^+$  using a PAS covering GC electrode is larger than the current value which doubled the current value observed with the curve (a) and the curve (c). This shows metal ion  $\text{Ag}^+$  working as quality of a reaction assistant, and promoting the oxidation-reduction reaction of PAS which is a conductive polymer compound. Moreover, when it moved into PC solution which does not contain  $\text{Ag}^+$  which dissolved  $\text{LiClO}_4$  for the electrode after obtaining the cyclic voltamogram shown with the curve (b) of [drawing 3](#) 0.1M as a supporting electrolyte and having been electrolyzed like the above, larger oxidation reduction current value than the current value which doubled (c) with the curve (a) like the curve (b) was observed.

[0049] Except having replaced with example 4Cu ( $\text{ClO}_4$ )<sub>2</sub>, and having used  $\text{FeCl}_3$ , it electrolyzed like the example 1 and curvilinear [ of [drawing 4](#) ] (a) - (c) was obtained, respectively. From the curve (b), the oxidation reduction potential of  $\text{Fe}^{3+}$  in a PAS covering GC electrode was observed by 0.3 volts on the basis of the normal hydrogen electrode. When curvilinear [ of [drawing 4](#) ] (a) - (c) is compared, the oxidation reduction current value [a curve (b)] obtained by electrolyzing the solution which contains metal ion  $\text{Fe}^{3+}$  using a PAS covering GC electrode is larger than the current value which doubled the current value observed with the curve (a) and the curve (c). This shows metal ion  $\text{Fe}^{3+}$  working as reaction adjuvant, and promoting the oxidation-reduction reaction of PAS which is a conductive polymer compound. Moreover, when it moved into PC solution which does not contain  $\text{Fe}^{3+}$  which dissolved  $\text{LiClO}_4$  for the electrode after obtaining the cyclic voltamogram shown with the curve (b) of [drawing 4](#) 0.1M as a supporting electrolyte and having been electrolyzed like the above, larger oxidation reduction current value than the current value which doubled (c) with the curve (a) like the curve (b) was observed.

[0050] Except having set PAS concentration in an example 5 cast solution to 10mM(s), having replaced with Cu ( $\text{ClO}_4$ )<sub>2</sub>, and having used the ferrocene, it electrolyzed like the example 1 and curvilinear [ of [drawing 5](#) ] (a) - (c) was obtained, respectively. From the curve (b), the oxidation reduction potential of the ferrocene in a PAS covering GC electrode was observed by 0.5v on the basis of the normal hydrogen electrode. When curvilinear [ of [drawing 5](#) ] (a) - (c) is compared, the oxidation reduction current value [a curve (b)] obtained by electrolyzing the solution which contains an organometallic compound ferrocene using a PAS covering GC electrode is larger than the current value which doubled the current value observed with the curve (a) and the curve (c). This shows an organometallic compound ferrocene working as quality of a reaction assistant, and promoting the

oxidation-reduction reaction of PAS which is a conductive polymer compound.

[0051] The poly aniline-Nafion complex covering GC electrode was created by carrying out the vacuum drying of the propanol-N-methyl-2-pyrrolidinone mixed solution (it being 4:1 at a capacity factor) containing the poly aniline of example 630mM, and Nafion after 3microl cast on a glassy-carbon (GC) electrode (area; 0.07cm<sup>2</sup>) for 1 hour. Using this electrode, it electrolyzed like the example 1 and curvilinear [ of drawing 6 ] (a) - (c) was obtained, respectively. In a curve (a), oxidation reduction is possible for poly aniline-Nafion complex in [ potential ] 0-+1.2 volts on the basis of a normal hydrogen electrode. The Cu<sup>2+</sup> oxidation reduction potential in a poly aniline-Nafion complex covering GC electrode was observed by 0.8 volts on the basis of the normal hydrogen electrode. When curvilinear [ of drawing 6 ] (a) - (c) is compared, the oxidation reduction current value [a curve (b)] obtained by electrolyzing the solution which contains metal ion Cu<sup>2+</sup> using a poly aniline-Nafion complex covering GC electrode is larger than the current value which doubled the current value observed with the curve (a) and the curve (c). This shows metal ion Cu<sup>2+</sup> working as reaction adjuvant, and promoting the oxidation-reduction reaction of the poly aniline-Nafion complex which is a conductive polymer compound.

[0052]

[Table 1]

実施例	1	2	3	4
導電性高分子化合物	スルホン化 ポリアニリン	スルホン化 ポリアニリン	スルホン化 ポリアニリン	スルホン化 ポリアニリン
反応補助物質	Cu <sup>2+</sup>	Cu <sup>2+</sup>	Ag <sup>+</sup>	Fe <sup>3+</sup>
支持電解質	LiClO <sub>4</sub>	LiClO <sub>4</sub>	LiClO <sub>4</sub>	LiClO <sub>4</sub>
支持電解質用溶媒	プロピレン カーボネート	プロピレンカ ーボネートと エチレンカー ボネート	プロピレン カーボネート	プロピレン カーボネート

[0053]

[Table 2]

実施例	5	6
導電性 高分子化合物	スルホン化 ポリアニリン	ポリアニリン ／ナフィオン
反応補助物質	フェロセン	$\text{Cu}^{2+}$
支持電解質	$\text{LiClO}_4$	$\text{LiClO}_4$
支持電解質用 溶媒	プロピレン カーボネート	プロピレン カーボネート

[0054] An example 7 poly aniline, and 2, 5-dimercapto - 1, 3, and 4-thiadiazole (DMcT) was dissolved in high concentration into the N-methyl-2-pyrrolidinone (NMP) solution, the copper ion was added further, and the viscous high ink-like solution was adjusted. This solution was applied on the conductive substrate (here copper sheet metal), and the poly aniline-DMcT-copper-ion complex thin film electrode with a thickness of 15-50 micrometers was produced by carrying out vacuum heating. The typical component ratio of this thin film is shown in Table 3.

[0055]

[Table 3]

成 分	重量比率 (%)
DMcT	43.2
$\text{Cu}^{2+} (\text{BF}_4^-)_2$	9.5
ポリアニリン	28.8
アセチレンブラック	7.2
残存溶媒 (NMP)	11.3

[0056] This thin film was made into the positive electrode, and the examination cell was assembled combining the metal lithium negative electrode and the polymer-gel electrolyte [500 micrometers in thickness which contains  $\text{LiBF}_4$  supporting electrolyte of 1.0M in an acrylonitrile-methyl acrylate copolymer, ethylene carbonate, and a propylene carbonate solvent (1:1-fold quantitative ratio)]. The charge-and-discharge characteristic curve as performed the repeat charge and discharge of an examination cell 10 times at 20 degrees C by 1.25C (charge-and-discharge speed which charges or discharges in all the 1C:electrode active materials in 1 hour) and shown with the curve (a) of drawing 7 was acquired. Moreover, the curve (b) of drawing 7 is a charge-and-discharge characteristic curve which has not added the copper ion and which was acquired on the same conditions by the poly aniline-DMcT complex electrode. By the system which added the copper ion, the 280 Ah/kg service-capacity-positive electrode and the average discharge voltage 3.3 V and energy-density [ of about 920Whs/kg ]-positive electrode were obtained. Moreover, although an oxidation-reduction reaction will become rate-limiting and a resistance component will appear in the case where a copper ion is not included if speed is gathered more than 1C, by adding a copper ion, high-speed charge and

discharge become possible, and also increase the stability in repeat charge and discharge further within [ in 1 hour ]. This shows that  $\text{Cu}^{2+}$  ion works as reaction adjuvant, and is promoting the oxidation-reduction reaction of poly aniline-DMcT.

[0057]

[Effect of the Invention] According to this invention, the oxidation-reduction reaction of the conductive polymer in which oxidation reduction is possible is promoted by reaction adjuvant, and the redox active electrode by which properties, such as charge-and-discharge speed and a speed of response of a sensor, were improved using the conductive polymer compound in which oxidation reduction is possible is obtained. Moreover, when the conductive polymer in which oxidation reduction is possible has the substituent combined with reaction adjuvant, it is stably fixed to the conductive polymer compound in which oxidation reduction is possible with high density, and high-capacity-izing of the redox active electrode using the conductive polymer compound in which oxidation reduction is possible as an electrode material, and the physical stabilization of reaction adjuvant are attained according to the amount of a substituent. Since the redox active electrode concerning this invention has the property which was excellent as mentioned above, it is suitable also as primary and the electrode of a rechargeable battery, the electrode for power storage, the counter electrode for electrochromic elements, the electrode for sensors and the catalyst electrode to various chemical reactions, and an optoelectric-transducer electrode.

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[Translation done.]